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This DURIP award has been issued for the acquisition of a scanning probe microscope system (SPM). Scanning Probe Microscopes are (SPMs) are used to probe material surfaces with atomic resolution. Unlike optical and electron microscopes, the SPMs reveal details not only in x- and y-directions but also along the z-axis, perpendicular to the surface. Typical lateral resolutions range from 20Å down to 1 Å, while in the vertical direction the resolution is better than 1Å. The main research objective supported by this system is the development of efficient bio-compatible actuators based on a novel polymer/metal composite. The scanning probe microscopy system was acquired using 33% matching funds from University of Arizona. The system was installed on August 31, 2001 and is currently operational.

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FINAL PERFORMANCE REPORT

TITLE: **MULTIMODE SCANNING PROBE MICROSCOPE SYSTEM FOR NANO-COMPOSITE ACTUATORS**
AFOSR GRANT F49620-01-1-0224

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Abstract

This DURIP award has been issued for the acquisition of a scanning probe microscope system (SPM). Scanning Probe Microscopes are (SPMs) are used to probe material surfaces with atomic resolution. Unlike optical and electron microscopes, the SPMs reveal details not only in x- and y-directions but also along the z-axis, perpendicular to the surface. Typical lateral resolutions range from 20Å down to 1 Å, while in the vertical direction the resolution is better than 1Å. The main research objective supported by this system is the development of efficient bio-compatible actuators based on a novel polymer/metal composite. Initial studies of this composite have shown large deformations under small actuation voltages. The reverse effect, the generation of electric signal as a result of mechanical deformation has also been demonstrated. These characteristics of the polymer composite can lead to the development of smart skins for reducing the wake behind bluff bodies, underwater and bio-medical micro-robots. The specific research objectives related to the acquired scanning probe microscopy (SPM) system are

- Develop an experimentally verified model with micro-structural parameters describing the composite actuator

- Measurement of surface potentials, cluster size as a function of the applied boundary conditions and solvent content and comparison with the prediction of the mode.

- Determine the relation between the electromechanical response and the microstructure of the polymer composite

- Development of more efficient electrochemical microactuators for use in ``smart skin" applications

The SPM microscope will also facilitate the research programs of Dr. Sridhar with NASA Johnson Space Center for development of Oxygen regeneration system as well as Dr. Wells from electrical engineering department for characterization of chemical mechanical polishing (CMP) process of Tungsten and Copper.

Status of effort:

The scanning probe microscopy system was acquired using 33% matching funds from University of Arizona. The system was installed on August 31, 2001 and is currently operational. A photograph of the installed system is shown in Figure 1.

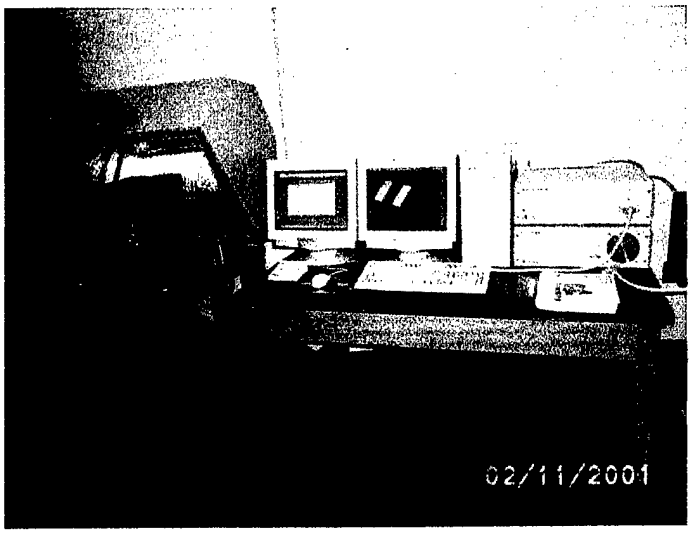

Figure 1 Scanning Probe Microscope

The SPM systems was purchased according to the initial proposal. A copy of the system components and their cost is enclosed in Table 1 below.

Table 1 SPM system components

Component	Model #	Cost
Nanoscope IIIA Scanning Probe Microscope Station	NS31-01	$72,000
NanoScope Multimode Atomic Force Microscope	MMAFM	$33,000
0.4μm AFM scanner for MMAFM	AS-0.5	$ 1,230
10μm AFM scanner for MMAFM, AFM and LFM	AS-12	$ 4,000
Cantilever Holder for scanning in Fluids with the Multimode AFM	MTFML	$3,000
Extender Electronics Module for Multimode AFM	PHASE-01	$8,000
Vibration Isolation Table fro the MMAFM	VT-102	$3,200
Dimension 3100 SPM	D3100	$ 23,000
Dimension AFM Scan Head	DAFM	$25,000
6-inch Vacuum Chuck for Dimension 3000 Series SPM	DSC-150	$ 2,500
Integrated Acoustin Enclosure for Dimension 3100 SPM	VT-103-3K	$11,500
Two Days Installation and Training	ITCS	$ 3,000
Additional on-site training for new systems	ITCSA	$ 2,000
Total Cost:		$ 191,430
University of Arizona Cost Sharing (33%)		($63,178)
Amount Requested from DURIP		$128,252

Summary of the research supported during the first year of use:
Two projects were supported during the first year of use. A short description of each follows:

Project #1: Nano-Composite Actuator Development

The main research objective supported by this system is the development of efficient bio-compatible actuators based on a novel electroactive polymer/metal composites. An electroactive polymer actuator consists of an ion-exchange membrane covered with a conductive layer. Various types of membranes are suitable. The most commonly used are perfluorinated sulfonic acid Nafion™, (DuPont, USA) which is a copolymer of tetra-fluoroethelene and perfluorinated monomers containing sulfonic acid groups. It is highly hydrophilic and is a strong polymeric acid. Its mechanical characteristics are similar to the ones of PTFE polymers such as Teflon. Ion-exchange membranes are used in hydrogen fuel cells and in the production of sodium or potassium hydroxide. When structured as a metal-polymer-metal composite they can also be used as an actuator. The polymer-metal composite actuator consists of a bulk region (the polymer) bounded by thin conductive metal interfaces. (See Figure 2 a.) The two metallic surfaces are highly conductive. Upon application of a potential difference at points A and B the cations in the bulk migrate towards the cathode dragging along water in the form of hydration shells. The large volume of the hydration shells causes local matrix expansion and deformation of the composite as shown in Figure 2 b.

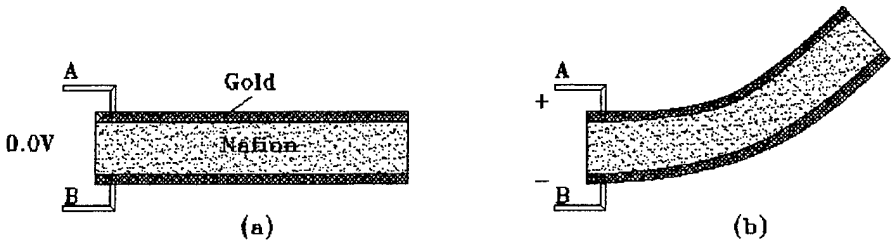

Figure 2 Polymer - Metal Composite Actuator

Fabrication

Metal-polymer composites can be produced by vapor or electro-chemical deposition of metal over the surface of the membrane. We have used an electrochemical platinization method [Fedkiw 1992]. The method consists of two steps: ion exchange of the protons H^+ with metal cations Pt^{2+} and chemical reduction of the ions onto the membrane surface with $NaBH_4$ solution. An SEM microphotograph of such a composite is shown in Figure 3. The electrode surfaces are approximately 0.8μm thick Pt deposits.

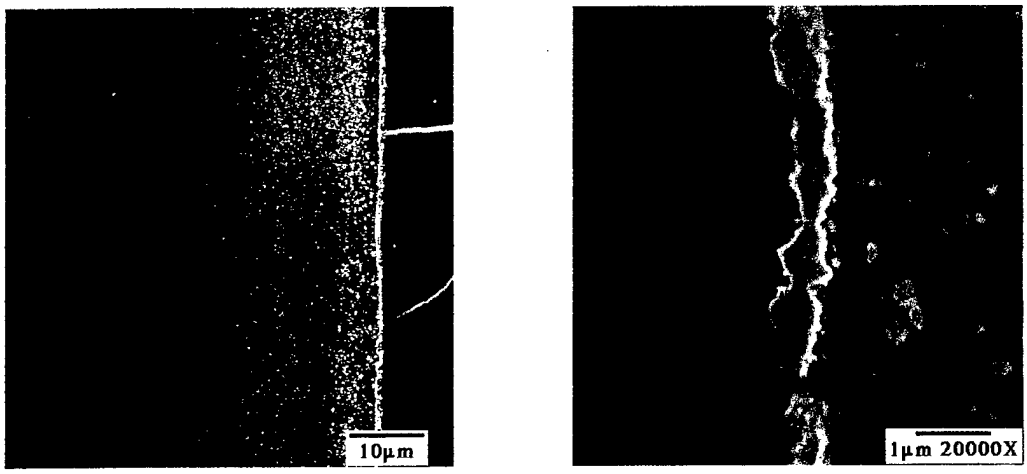

Figure 3 Nafion membrane with Pt electrodes on each side

Mathematical model

Electrochemical studies on Nafion™ and similar membranes have shown that water transport is actually responsible for their swelling [Eikerling 1998]. In the presence of water the polar sulfonic or carboxilic cites dissociate and produce fixed anionic groups and mobile H^+ ions. These protons become hydrated, and under an external electric field are able to migrate. The process is complicated because of the porous microstructure of the polymer matrix [Helfferich 1962]. In a humid environment the water penetrates towards the ionogenic sites inducing swelling of the hydrophilic pores. Under water depletion conditions these pores collapse. As a result, the permeability coefficient in the Darcy's law for water flux is dependent on the water content [Eikerling 1998]. In dry environments the actuator performance is greatly reduced. A schematic representation of the ionic processes taking place inside the polymer is shown in Figure 4. The external electric field generates a flux of hydroxonium ions towards the cathode. At the cathode these ions pick up an electron and produce hydrogen and a free water molecule. On the anodic side water molecules dissociate producing oxygen and hydroxonium ions. The re-distribution of water within the membrane creates local expansion of the plymer matrix. Associated with it is a gradient of the internal (osmotic) pressure. This gradient generates a flux of free water in the opposite direction, governed by a law that is macroscopically similar to Darcy's law for pressure driven flow in porous media [Hassanizadeh 1986].

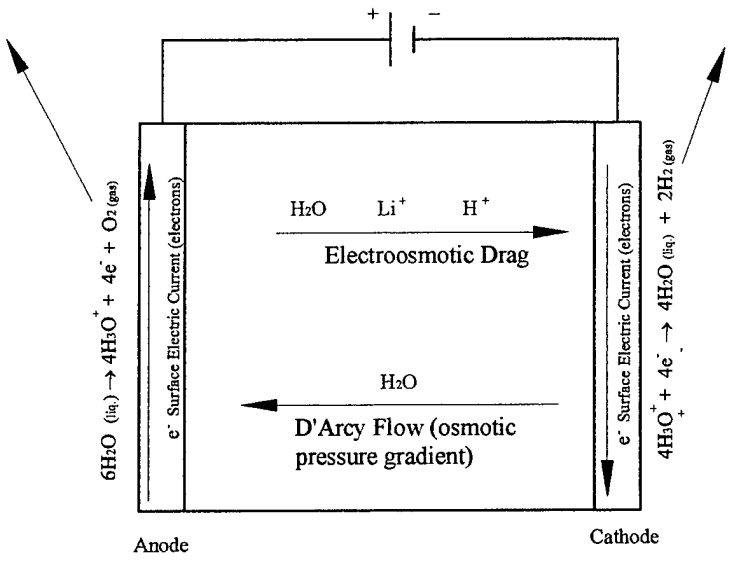

Figure 4 Transport model

The total deformation of the polymer matrix is decomposed in two additive parts: elastic deformation of the polymer network due to external forces or fields (mechanical, electrical), resulting in elastic strain γ_{ij}^{elast} and deformation due to re-distribution of ions and solvent which we call chemical strain and denote by γ_{ij}^{chemt}. The chemical strain is related to the compositional variables through $\gamma_{ij}^{chem} = \rho_0 \sum_s \frac{\overline{\vartheta}^s}{3\mathcal{M}^s}\left(c^s - c_0^s\right)\delta_{ij}$, where $\overline{\vartheta}^s$ are the partial molar volumes and c^s are the mass fractions. Thus the total strain is given by

$$\gamma_{ij} = \gamma_{ij}^{elast} + \rho_0 \sum_s \frac{\overline{\vartheta}^s}{3\mathcal{M}^s}\left(c^s - c_0^s\right)\delta_{ij}$$

The elastic behavior of the polymer matrix can has been previously modeled by a Mooney-Rivlin material [Shahinipoor 1993]:

$$\psi^{elast} = C_1(I_1 - 3) + C_2(I_2 - 3),$$

where I_1 and I_2 are the first and second principle invariants of the Green's deformation tensor, C_1 and C_2 are temperature dependent elastic constants. For example, for rubbery materials Treloar derived [Treloar 1958] $C_1 = \frac{\mathcal{R}T}{2\mathcal{M}_c}$, where $\mathcal{M}_c$ is the number average chain molecular weight. The complete the model requires establishment of laws between the thermodynamic fluxes and corresponding driving forces. The basis for these laws is the reduced entropy production inequality. Based on the entropy production due to diffusive heat transport and chemical reactions respectively, the linear Onsager theory results in the usual Fourier heat conduction law as well as activity driven reaction kinetics. For the sake of brevity these will not be discussed here. Due to the inclusion of chemical strains, the gradient of the electrochemical potential includes not only gradients of mass fractions and electric field, but also an gradients in osmotic pressure responsible for the relaxation of the actuator under constant electric field. The resulting expressions are

$$\mathbf{J}^s = -c^s \mathcal{W}^s \nabla\left(\mu^s + Z\phi\right)$$

$$\text{where } \mu^s = \mathcal{F}^s - \mathcal{N}^s \Delta T + \frac{\mathcal{R}T}{\mathcal{M}^s} \ln f^s c^s + \frac{p\mathcal{V}^s}{\mathcal{M}^s}$$

where $\mathcal{W}^s$ is the molar mobility of component s, μ^s is the chemical potential and ϕ is the electric potential.

Experimental measurements

Tapping mode AFM scan of 90nm x 90nm area of the surface of a Nafion™117 sheet is shown in Figure 5. The initial data suggest that the 5-10nm features correspond to the hydrophilic regions responsible for the water transport. This conjecture will be further investigated in the future using phase and surface potential measurements.

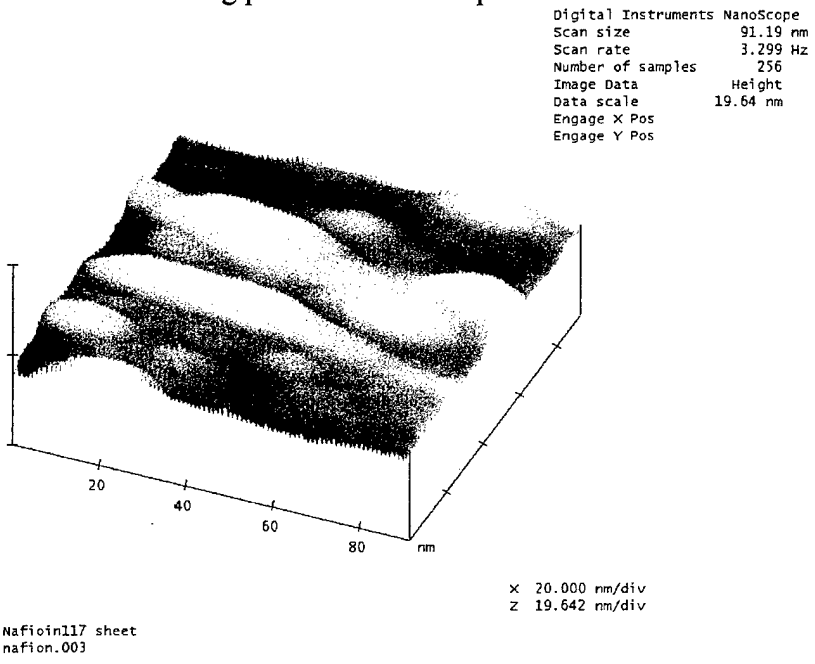

Figure 5 Topography scan of Nafion 117, using tapping mode AFM

Additional investigations of the nano-structure of the composite along with a theoretical model development is required in order to predict and improve the energy conversion efficiency of these actuators. Among the technological challenges to be overcome is the development of surface coating, preventing water diffusion and thus allowing for use in dry environments.

Project #2: Charge writing for electrostatic assembly of proteins

The availability today of sophisticated instrumentation used for nanotechnology applications has now made it possible to investigate in the nanometer scale the surface-protein and protein-platelet interactions as influenced by surface charge distribution. Scanning probe microscopy-based lithography can now be used to create specific and well-defined charge distribution on specific surface sites, and the resulting electric force field and the protein and platelet adhesions can now be imaged using atomic force microscopy (AFM). The specific aims of this study are: (1) To determine the effect of several surface charge distributions on the binding and conformation of fibrinogen and collagen molecules; (2) To determine the

effect of surface charge distributions on the polymerization of fibrinogen and collagen into fibrin as mediated by thrombin. The acquired SPM system was tested and initial test measurements were performed using tapping mode AFM, Surface Potential and Electric Force microscopy. Several samples were imaged successfully – atomic planes of freshly cleaved mica, silicon and a glass substrate with an array of conductive Indium Tin Oxide (ITO) electrodes. To demonstrate the surface potential measurement technique, we have measured the residual potential resulting from charge trapped at the ITO/silicon nitride interface. The samples were coated with PECVD silicon nitride and imaged after a application of a single voltage step of 400V for 10 seconds. The resulting topography and residual surface potential are shown in Figure 6 a. and b. respectively.

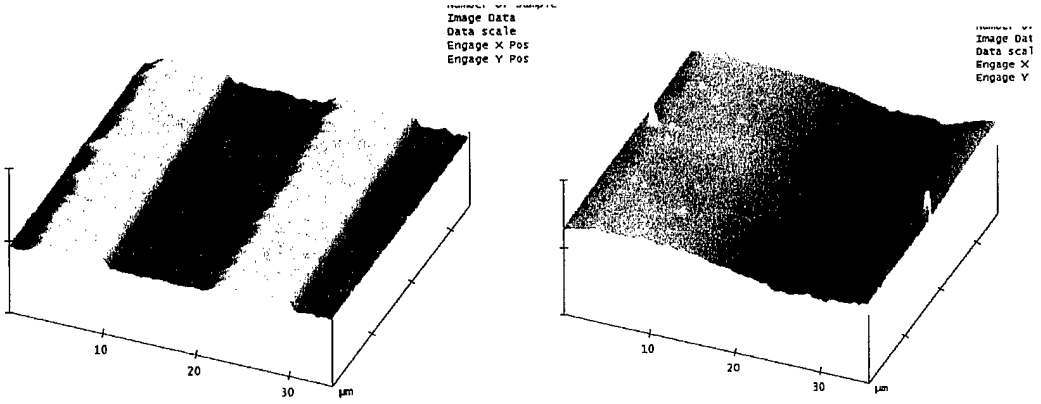

Figure 6 a. Topography image (left); b. Residual surface potentail (right)

Further tapping mode AFM imagines of collagen immobilized on mica sheets has also been performed. Figure 7 shows a scan of two individual collagen molecules attached to the surface via BSA proteins.

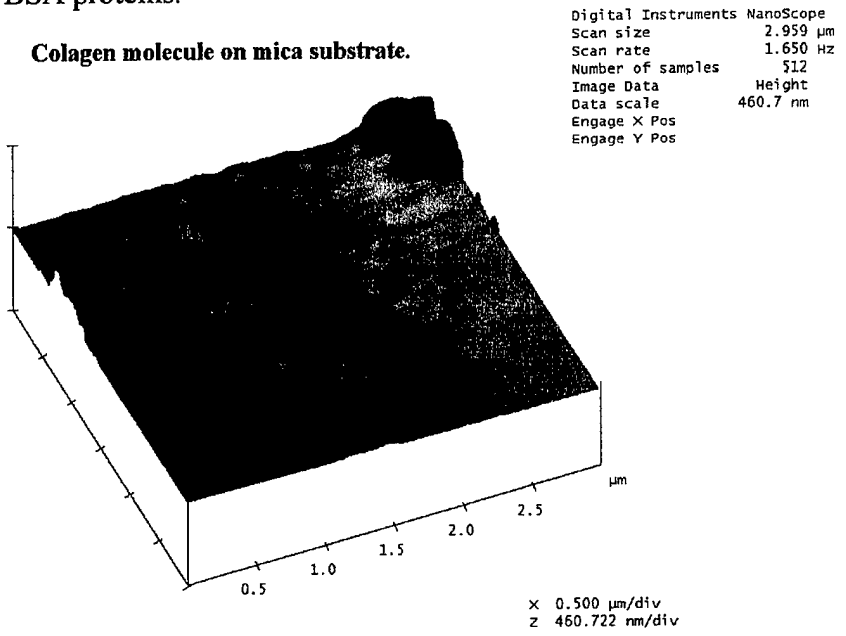

Figure 7 Collagen molecules on mica substrates (gray areas are BSA molecules)

Personnel Supported
Graduate Students: Mr. Kalin Lazarov, Mr. Geon Seo

Publications
Enikov, E. T., Seo, G., and Nelson, B.J., "Mechanics of Ion-Exchange Polymer/Metal Composite Actuators," Smart Materials and Structures, March 2002 (under review).

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